

CD221. LECTURE 5. PHYSICAL SIGNIFICANCE OF T, P, μ .

We've now learnt how to *formally* solve the fundamental problem of thermodynamics, meaning, we now know what equations need to be solved to tell us the final equilibrium state that a composite system will evolve to after its internal constraint is released. But we won't be able to get actual numbers out of this formal solution unless we know the exact form of the fundamental relation for the system in question. And that's something only statistical mechanics can tell us.

In showing how to solve the fundamental problem of thermodynamics, we also learnt that when two systems are in thermal equilibrium, they both have the same value of the parameter $T = (\partial U / \partial S)_{V,N}$. That is, the state of thermal equilibrium is defined by the condition

$$T_1^{(f)} = T_2^{(f)} \quad (1)$$

• We'll now see if this parameter has a meaningful physical interpretation. To this end, we'll examine the special case of a closed composite system (of fixed V and N as in the previous example) that starts out with T in sub-system 1 being *greater* than T in sub-system 2. In other words, for this system let's arrange matters so that $T_1 > T_2$ initially.

When the system's internal constraint is now made diathermal, the overall change in entropy ΔS is the sum of the entropy changes in 1 and 2, i.e.,

$$\Delta S = \Delta S_1 + \Delta S_2 > 0 \quad (2)$$

(The use of Δ in these equations rather than d is meant to indicate that the changes that occur following the release of the internal constraint need not be infinitesimal.) The energy changes accompanying these entropy changes are given by $\Delta S_1 = \Delta U_1 / T_1$ and $\Delta S_2 = \Delta U_2 / T_2$. (These results follow from writing $(\partial S / \partial U)_{V,N} = 1/T$ as $dS = dU / T$ and then integrating under the assumption that T is approximately a constant.) Again, from the principle of energy conservation, $\Delta U_1 = -\Delta U_2$, so Eq. (2) becomes

$$\Delta S = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Delta U_1 > 0 \quad (3)$$

Since $T_1 > T_2$, the term in parentheses in Eq. (3) is negative, which means that ΔU_1 has to be negative too to satisfy the inequality. This in turn means that the sub-system with the higher T loses energy (specifically heat, because no work is done during the change) to the sub-system with the lower T . We know from everyday experience that it's *hot* objects that lose heat when placed in contact with cold objects, and we also know that a

measure of hotness or coldness of these objects is their temperature. So based on this information, we'll now identify T with this quantity called temperature, more specifically the *absolute* temperature. The significance of the qualifier absolute will become clear shortly.

What Eq. (1) tells us, then, is that when systems are in thermal equilibrium with each other, their temperatures are the same.

- We also said – postulated actually – that the entropy tends to increase as energy increases, specifically that the entropy is a monotonically increasing function of the energy. In mathematical language, we can express this property as

$$\left(\frac{\partial S}{\partial U} \right)_{V,N} > 0 \quad (4)$$

which means that

$$\frac{1}{T} > 0 \quad (5)$$

or that $T > 0$. And having earlier identified T with temperature, this in turn means that temperatures must be positive.

So T in these relations is obviously *not* the temperature that we refer to when we discuss, say, the daily weather. That temperature is what we measure with a thermometer, a thermometer being any device that responds to the flow of heat into or out of it by a change in just *one* of its macroscopic properties. A column of mercury in a narrow sealed glass capillary is one such thermometer, the length L of the mercury column acting as the thermometric parameter. When a thermometer of this kind is placed in thermal contact with some system A , and allowed to reach equilibrium, the corresponding thermometric parameter assumes some value, say θ_A , which we'll call the *thermometric* temperature of A with respect to that thermometer. The same thermometer placed in thermal contact with another system B might yield a reading of θ_B . If $\theta_A \neq \theta_B$, experience tells us that placing A in thermal contact with B will lead to an exchange of heat, the system with the higher value of θ losing heat to the system with the lower value of θ , until, eventually, at equilibrium, $\theta_A = \theta_B$.

If a thermometer with a *different* thermometric parameter (electrical resistance R , for instance, instead of length L) were used to make the measurements, the temperature of A might now be θ'_A , and that of B might be θ'_B . But it would still be the case that $\theta'_A = \theta'_B$ when A and B are thermally equilibrated with each other. In other words, *two systems will remain in equilibrium when placed in thermal contact with each other if and only if they have the same temperature with respect to the same thermometer.*

But suppose the thermometric parameter is $(\partial U / \partial S)_{V,N}$, or equivalently $(\partial S / \partial U)_{V,N} \propto \Omega^{-1}(\partial \Omega / \partial U)_{V,N}$, which is the fractional increase with energy of the number of microstates; in this case, every thermometer, of whatever kind, must yield the same value of this parameter, viz., T , when it is used to measure the temperature of a particular system. In other words, if T_A is the *thermodynamic* temperature of A as measured by one thermometer and T'_A is its temperature as measured by another, it must be the case that $T_A = T'_A$ (even though, in general, $\theta_A \neq \theta'_A$.) If it were not, then in principle one could have a situation where two different systems A and B were in thermal equilibrium and yet did not satisfy $T_A = T_B$, which would violate Eq. (1). It is for this reason that the temperature T is called an absolute temperature, and by convention, the units of this temperature are called degrees Kelvin, symbolized °K.

- Furthermore, Postulate IV tells us there is a smallest temperature, viz., 0, which is the temperature at which the entropy vanishes. A temperature of 0 °K is called absolute zero. But how do we assign numerical values to temperatures away from absolute zero? One way is to determine it from any theoretical relation that describes a real system and that includes T in it. There are many such relations describing gases that can be used for this purpose, but we won't discuss them further. For the moment, we'll only note that the absolute or Kelvin scale of temperatures is established by assigning a definite value of T to a chosen standard system. By an international agreement adopted in 1954, this system is taken to be water at its triple point, i.e., water under conditions in which all of its three states of aggregation mutually exist in equilibrium. At the triple point of water, T is chosen to have the value

$$T_t = 273.16 \text{ }^\circ\text{K} \quad (\text{exactly})$$

This seemingly strange value was chosen to ensure that the absolute scale of temperature agreed with other earlier temperature scales, which used other thermometric parameters and were based on other conventions.

- The definition $T = (\partial U / \partial S)_{V,N}$ implies that the dimensions of T are defined by the dimensions of energy and entropy. We don't really know how to fix the dimensions of entropy, but we do know that entropy is also determined by the Boltzmann relation, $S = k_B \ln \Omega$, which means that its dimensions are determined by those of the Boltzmann constant, which at the moment we don't know either. As a matter of convention, therefore, we'll choose the entropy to be *dimensionless*, and this implies that the dimensions of temperature are just those of energy. These quantities have different units, of course, energy being expressed in Joules and temperature in degrees Kelvin. k_B , then, is the conversion factor between these units, which must therefore also be a universal constant. Its value has been determined (again, we won't discuss how right now), and is given by

$$k_B = 1.3806 \times 10^{-23} \text{ J / K}$$

The product of k_B and T , viz., $k_B T$ is therefore an energy, and it defines a fundamental scale of energy that is relevant to single atoms and molecules, as we'll see later.

- We can make a connection between entropy and heat too. In any infinitesimal change of the kind we've been considering, where only energy U is exchanged, not V or N , the change in entropy can always be written quite generally as

$$dS = S(U + dQ, V, N) - S(U, V, N) \quad (6)$$

A Taylor expansion of the first term on the RHS leads to the following result:

$$\begin{aligned} dS &= S(U, V, N) + \left(\frac{\partial S}{\partial U} \right)_{V, N} dQ - S(U, V, N) \\ &= \frac{1}{T} dQ \end{aligned} \quad (7)$$

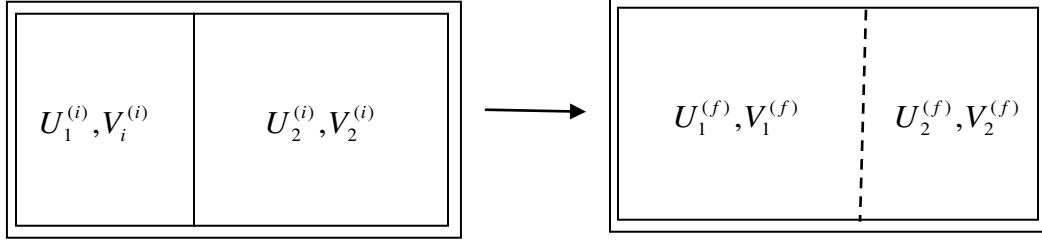
which tells you that entropy is effectively heat.

The Parameters P and μ

Just as the derivative $(\partial U / \partial S)_{V, N}$ was found to have a definite physical meaning in terms of the temperature, so also can the other derivatives appearing in the differential form of the fundamental relation, viz., $(\partial U / \partial V)_{S, N}$ and $(\partial U / \partial N)_{S, V}$, be found to be physically meaningful and to be expressible in terms of other well-known, familiar concepts. Let's see how by examining a closed composite system in which contact between the two sub-systems can be effected by both thermal and mechanical interactions.

• Systems in Thermal and Mechanical Contact

Consider a composite whose macrostates are defined by energy and volume alone (N being assumed to remain constant during the course of any changes the system may be made to undergo). The arrangement is as in the left panel below. If the internal constraint in this arrangement is now made diathermal *and* moveable, what happens? The new states that result are shown in the right panel:



Now the problem is to find the values of 4 unknowns: $U_1^{(f)}$, $U_2^{(f)}$, $V_1^{(f)}$ and $V_2^{(f)}$ (assuming that the initial values of these parameters are known.) For this we need 4 equations. We can immediately write down two:

$$U_1^{(f)} + U_2^{(f)} = U \quad (8)$$

and

$$V_1^{(f)} + V_2^{(f)} = V \quad (9)$$

where U and V are, respectively, the total energy and total volume of the composite system, which remain fixed during the change of state, and which are assumed known. To get two more equations in the unknowns, we invoke our thermodynamic postulates, starting with

$$S^{(f)} = S_1^{(f)} + S_2^{(f)}, \quad (\text{Postulate III}) \quad (10)$$

We next note that $dS^{(f)} = 0$ by entropy maximization, and so

$$dS_1^{(f)} = -dS_2^{(f)}, \quad (\text{Postulate II}) \quad (11)$$

Further, because the entropies of 1 and 2 are functions of $U_1^{(f)}$, $U_2^{(f)}$, $V_1^{(f)}$ and $V_2^{(f)}$ (Postulate III), we can use Taylor's expansions to write

$$dS_1^{(f)} = \left(\frac{\partial S_1^{(f)}}{\partial U_1^{(f)}} \right) dU_1^{(f)} + \left(\frac{\partial S_1^{(f)}}{\partial V_1^{(f)}} \right) dV_1^{(f)} \quad (12a)$$

and

$$dS_2^{(f)} = \left(\frac{\partial S_2^{(f)}}{\partial U_2^{(f)}} \right) dU_2^{(f)} + \left(\frac{\partial S_2^{(f)}}{\partial V_2^{(f)}} \right) dV_2^{(f)} \quad (12b)$$

Recall that at constant N , $dS = (1/T)dU + (P/T)dV$ in general, and hence

$$dS_1^{(f)} = \frac{1}{T_1^{(f)}} dU_1^{(f)} + \frac{P_1^{(f)}}{T_1^{(f)}} dV_1^{(f)} \quad (13a)$$

and

$$dS_2^{(f)} = \frac{1}{T_2^{(f)}} dU_2^{(f)} + \frac{P_2^{(f)}}{T_2^{(f)}} dV_2^{(f)} \quad (13b)$$

Substituting Eqs. (13a) and (13b) into Eq. (11), along with the relations $dU_1^{(f)} = -dU_2^{(f)}$ and $dV_1^{(f)} = -dV_2^{(f)}$, which reflect the constancy of U and V , we arrive at

$$\left(\frac{1}{T_1^{(f)}} - \frac{1}{T_2^{(f)}} \right) dU_1^{(f)} + \left(\frac{P_1^{(f)}}{T_1^{(f)}} - \frac{P_2^{(f)}}{T_2^{(f)}} \right) dV_1^{(f)} = 0 \quad (14)$$

To satisfy this equation for arbitrary values of the changes $dU_1^{(f)}$ and $dV_1^{(f)}$, it is necessary that

$$T_1^{(f)}(U_1^{(f)}, V_1^{(f)}) = T_2^{(f)}(U_2^{(f)}, V_2^{(f)}) \quad (15a)$$

and

$$P_1^{(f)}(U_1^{(f)}, V_1^{(f)}) = P_2^{(f)}(U_2^{(f)}, V_2^{(f)}) \quad (15b)$$

These two equations, together with Eqs. (8) and (9), constitute a set of 4 equations in 4 unknowns, which can be solved, thereby solving the thermodynamic problem.

• The parameter P

In the same way that we identified T with temperature, we can similarly get a handle on the physical meaning of P by considering the direction of “volume flow” in a closed composite system (of fixed N) that starts out with $P_1 > P_2$ and $T_1 = T_2 = T$. After the internal constraint is released and the system settles into a new equilibrium state

$$\Delta S = \Delta S_1 + \Delta S_2 > 0 \quad (16)$$

The energy and volume changes accompanying these entropy changes are given by $\Delta S_1 = \Delta U_1 / T + P_1 \Delta V_1 / T$ and $\Delta S_2 = \Delta U_2 / T + P_2 \Delta V_2 / T$. (These results follow from integrating $dS = dU / T + P dV / T$ under the assumption that T and P are constants, independent of U and V .) Since $\Delta U_1 = -\Delta U_2$ and $\Delta V_1 = -\Delta V_2$, Eq. (16) becomes

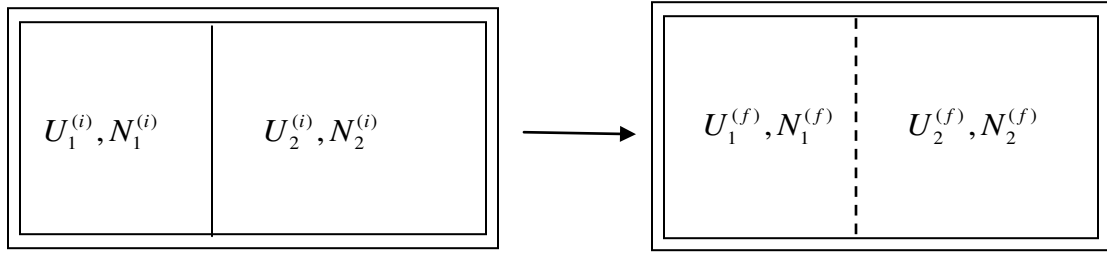
$$\Delta S = \frac{1}{T}(P_1 - P_2)\Delta V_1 > 0 \quad (17)$$

Since $P_1 > P_2$, the inequality is satisfied only if $\Delta V_1 > 0$, which means that sub-system 1 expands, and volume “flows” into sub-system 2. This is the expected behavior if P is identified with pressure, since systems with higher pressure tend to push out against systems with lower pressure.

Thus, when systems are placed in thermal and mechanical contact, energy and volume flow so as to equalize temperatures and pressures (maximizing entropy.)

• Systems in Thermal and Chemical Contact

If the internal constraint in a closed composite system is made diathermal and *permeable* (but not moveable), the resulting change of state can be depicted schematically as



and our thermodynamic postulates along with energy and mole number conservation can be shown to lead to the following 4 equations in 4 unknowns (*please show this*):

$$U_1^{(f)} + U_2^{(f)} = U \quad (18a)$$

$$N_1^{(f)} + N_2^{(f)} = N \quad (18b)$$

$$T_1^{(f)}(U_1^{(f)}, N_1^{(f)}) = T_2^{(f)}(U_2^{(f)}, N_2^{(f)}) \quad (18b)$$

$$\mu_1^{(f)}(U_1^{(f)}, N_1^{(f)}) = \mu_2^{(f)}(U_2^{(f)}, N_2^{(f)}) \quad (18c)$$

The solution of these equations solves the thermodynamic problem.

- The parameter μ

You can show (please do this) that μ can be identified with the chemical potential, and that systems with higher chemical potential tend to transfer matter to systems with lower chemical potential.

Thus, when systems are placed in thermal and chemical contact, energy and matter flow so as to equalize temperatures and chemical potentials (maximizing entropy.)

- Some mathematical consequences

(i) We showed earlier that S is an extensive variable by virtue of it being additive. This additivity property was postulated on the basis of the additivity of U , which we assumed, and from which U 's own extensivity follows. The extensivity of U also means that

$$\lambda U(S, V, N) = U(\lambda S, \lambda V, \lambda N), \quad \lambda > 0 \quad (19)$$

If this expression is differentiated with respect to λ using the chain rule, we get

$$\begin{aligned} U &= \frac{\partial U}{\partial \lambda S} \frac{\partial \lambda S}{\partial \lambda} + \frac{\partial U}{\partial \lambda V} \frac{\partial \lambda V}{\partial \lambda} + \frac{\partial U}{\partial \lambda N} \frac{\partial \lambda N}{\partial \lambda} \\ &= \frac{\partial U}{\partial \lambda S} S + \frac{\partial U}{\partial \lambda V} V + \frac{\partial U}{\partial \lambda N} N \end{aligned} \quad (20)$$

λ is arbitrary, so it can be set to 1. When this is done, and the partial derivatives in the above expression replaced by their definitions in terms of T , P and μ , the result is the Euler equation

$$U = TS - PV + \mu N \quad (21)$$

which is an integrated form of the differential expression for the fundamental equation. If you recall that T , P and μ are themselves functions of S , V and N , it should now be clear why knowledge of 3 equations of state (and not just one or two) is equivalent to knowing the fundamental equation itself.

(ii) The Euler equation leads to another equation, the Gibbs-Duhem equation, which is derived as follows: Start by taking the differential of Eq. (21). This leads to

$$dU = d(TS) - d(PV) + d(\mu N) \quad (22)$$

To simplify the RHS, consider $d(TS)$ as an example. By definition it is the small difference between the new and old values of TS , which is

$$\begin{aligned}
d(TS) &= (T + dT)(S + dS) - TS \\
&= TS + TdS + SdT + dTdS - TS \\
&= TdS + SdT
\end{aligned} \tag{23}$$

The last line in Eq. (23) follows from the fact that $dTdS$ is much much smaller than the other terms, and can therefore be discarded. If the other terms in Eq. (22) are treated the same way, the result is

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu \tag{24}$$

We know another expression for the differential of U ; it is

$$dU = TdS - PdV + \mu dN \tag{25}$$

If we subtract Eq. (25) from Eq. (24), we now get

$$0 = SdT - VdP + Nd\mu$$

or equivalently,

$$Nd\mu = -SdT + VdP \tag{26}$$

which is the Gibbs-Duhem equation. It is an equation between 3 *intensive* variables (intensive variables being those that don't change with the size of the system), and it implies that they cannot all be varied independently. Two of them can, but then the third is fixed.

By dividing Eq. (26) by N , we get the molar form of the Gibbs-Duhem equation:

$$d\mu = -sdT + vdP \tag{27}$$

These various thermodynamic relations will be helpful as we next turn to the application of the Boltzmann equation to the evaluation of the fundamental equation of a specific model system.